



RE APPLICATION OF

FOR

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Claude Couture, et al.

**CROSSLINKED POLYSACCHARIDE,  
OBTAINED BY CROSSLINKING WITH  
SUBSTITUTED POLYETHYLENE GLYCOL, AS  
SUPRABSORBANT**

10/044,846

November 09, 2001

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February 20, 2002

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AUG 08 2002  
TC 1700

**TRANSMITTAL LETTER OF 35 U.S.C. § 119  
FOREIGN PRIORITY DOCUMENTS**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

Applicants hereby claim priority under 35 U.S.C. § 119 for the above-identified U.S. patent application. This claim of priority is based upon Canadian Application for Patent Serial No. 2,325,643, filed 10 November 2000 and Canadian Application for Patent Serial No. 2,351,253, filed 26 June 2001.

**CERTIFICATE OF MAILING**

I hereby certify that this TRANSMITTAL LETTER OF 35 U.S.C. § 119 FOREIGN PRIORITY DOCUMENT and all document indicated therein as being enclosed are being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231 on April 18, 2002

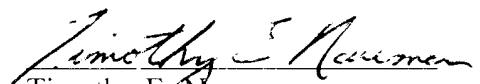
By: Mary M. Schriner  
Mary M. Schriner

Date: April 18, 2002

As required by paragraph 2 of 35 U.S.C. §119, enclosed herewith are certified copies of Canadian Application for Patent Serial No. 2,325,643, filed 10 November 2000 and Canadian Application for Patent Serial No. 2,351,253, filed 26 June 2001.

Respectfully submitted,

FAY, SHARPE, FAGAN,  
MINNICH & MCKEE, LLP

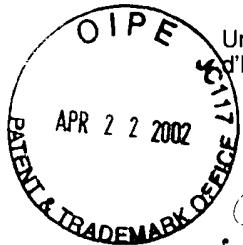


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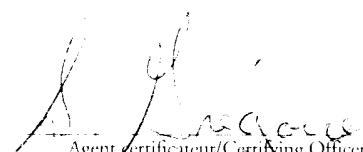
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the Patent Office.

Specification and Drawings, as originally filed, with Application for Patent Serial No: 2,351,253, on June 26, 2001, by **GROUPE LYSAC INC./LYSAC GROUP INC.**, assignee of Claude Couture, David Bergeron and Frédéric Picard, for "Crosslinked Polysaccharide, Obtained by Crosslinking with Substituted Polyethylene Glycol, as Superabsorbent".

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(CIPO 68)  
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ABSTRACT

5 New crosslinked polysaccharides useful as absorbents alone or in a mixture are obtained by reacting polysaccharides with at least one crosslinker selected in the group constituted by halogenated (Cl, Br, I), mesylated, tosylated, or triflated polyethylene glycol.

**CROSSLINKED POLYSACCHARIDE, OBTAINED BY CROSSLINKING  
WITH SUBSTITUTED POLYETHYLENE GLYCOL, AS  
SUPERABSORBENT**

5 The present invention relates to new reticulated polysaccharides obtained from polysaccharides by crosslinking with at least one crosslinker selected in the group constituted by substituted (preferably halogenosubstituted, more preferably substituted by Br, Cl or I) polyethyleneglycols.

10 The present invention also relates to processes for preparing said crosslinked polysaccharides.

15 The present invention also relates to the use of the crosslinked polysaccharides of the invention as superabsorbents, more particularly as inexpensive and/or hypoallergenic biodegradable superabsorbents.

The invention also relates to superabsorbents mixtures comprising at least one of crosslinked polysaccharides of the invention.

20 BACKGROUND OF THE INVENTION

Anbergen and Oppermann<sup>1</sup> have studied the elasticity and the swelling behaviour of sodium carboxymethylcellulose and hydroxyethylcellulose, chemically crosslinked with divinylsulfone 1.

5 In a patent issued in 1995, Kabra<sup>2</sup> reported the sorption capacity of hydroxypropylcellulose, crosslinked with different concentration of divinylsulfone (from 0.28 to 2.98 weight %). His best result showed a water sorption capacity of 44 g/g with a crosslink of 0.91 weight %. The author also mentions that other hydrophobically modified carbohydrate polymers can be chosen, such as hydroxypropylstarch.

10

More recently, a patent has been granted to SCA Hygiene Products AB<sup>3</sup> which extends the study with divinylsulfone to low-cost, readily available, renewable starting materials such as carboxymethylcellulose, carboxymethylstarch, and others. According to the authors, results may be obtained with a mixture of carboxymethylcellulose: hydroxyethylcellulose (3 : 1) which absorbs close to 95 g of synthetic urine per g of polymer after free swelling for 120 min. In this patent, however, the quantity of divinylsulfone used is not reported. The same company has extended their work with divinylsulfone to other polysaccharides containing acidic groups<sup>4</sup>. It appears that the best result was obtained with carboxymethylcellulose crosslinked with 14 mol% of divinylsulfone. This results in a centrifugal retention capacity of 111 g/g with synthetic urine. On page 6 of the patent<sup>4</sup>, it mentionned that the superabsorbent polysaccharides combine high absorption capacity with control of bacterial growth and control of odour, as well as with biodegradability. There is however no evidence that such compounds

20

would be biodegradable, particularly since it is well known that carboxymethylcellulose and carboxymethylstarch are not completely biodegradable. Moreover, it appears that the diethylsulfone diether linkage is not biocompatible.

5 Therefore, there is still a need for new polysaccharide-based superabsorbents with a significant biodegradability.

#### DESCRIPTION OF THE INVENTION

10

The new reticulated polysaccharides according to the invention are obtained by crosslinking of a polysaccharide with at least one substituted polyethylene glycol.

15

A preferred embodiment of the invention is constituted by reticulated starches obtained by crosslinking starches with at least one polyethylene glycol. As a matter of exemplification, starches crosslinked with dichloropolyethylene oxide are preferred particularly since starch is a renewable and inexpensive starting material.

20

The reticulated starches according to the invention are characterized by reticulation occurring at first on the OH group on the C6 carbon atom of the polymeric unit, then on a C2 or C3 carbon atom of the polymeric polysaccharide.

The crosslinker used for preparing the crosslinked starches of the invention is a substituted polyethylene glycol.

Polyethylene glycol (PEG<sub>2</sub>) has been used in blended starches for specific applications<sup>5-9</sup>. Starch can react with ethylene glycol in the presence of an acid catalyst at elevated temperature to yield crude mixtures of glycol glucosides by cleavage of glycosidic bonds<sup>10,11</sup>. By high energy radiation, it is possible to link poly(ethylene oxide) to starch<sup>12</sup>. It has also been reported that starch dialdehyde reacts with polyethylene glycol to give an acetal functionality<sup>13</sup>; Ethylene oxide can be grafted to starch by anionic polymerization<sup>14,15</sup> and polyethylene glycol chloroformate derivative<sup>16</sup> or ethylene glycol chloroformate<sup>17</sup> can also be used to crosslink starch. Moreover, diglycidyl ether<sup>18</sup>, polyglycidyl ethers<sup>19</sup> and ethylene glycol dimethacrylate<sup>20</sup> are among known crosslinkers.

Polyethylene glycols are biodegradable aerobically and anaerobically<sup>21</sup>.

Starches crosslinked with dichloro polyethylene oxides 3 appear to be biodegradable. The study of the crosslinker length was performed by preparing dichloro derivatives of di 4, tri 5 and tetra ethylene oxide 6 (SOCl<sub>2</sub>, pyridine, benzene, reflux). The experimental result thereby obtained show that carboxymethylstarch crosslinked with 0.62% of divinylsulfone 7, gives a water retention of 23 g/g in 0.9% saline solution, compared to 30 g/g when crosslinked with 9.85% of dichlorotriethylene dioxide 8. The starch-citraconic half ester crosslinked with 0.6% of divinylsulfone 9 were found to

exhibit a good water retention (25 g/g). The effect of divinylsulfone and dichlorotriethylene dioxide concentrations on the water retention of crosslinked carboxymethylstarch in 0.9% saline solution, are shown on figures 1 and 2. Even if 15 times more quantity of dichlorotriethylene dioxide is required to reach the maximum water retention, the choice of the former is still advantageous since divinylsulfone is very expensive.

5 Crosslinked carboxymethylstarches (figures 1 and 2) are prepared in two steps.

10 Starch is first alkylated with chloroacetic acid, thus the alkylated starch thereby obtained is crosslinked.

15 The applicant has also discovered that it is possible to perform the crosslinking before the alkylation without negative effect on the water retention.

One important aspect is to prepare starch derivatives without starch gelatinisation. This result was achieved with a lower pH with NaOH 3%, lower temperature and by adding sodium chloride solution.

20 Other polyethylene glycol derivatives may be used as crosslinkers. For instance, other dihalides (Br, I) could be prepared as well as dichloroformates derivatives 10; diacyl chloride derivatives 11 and; diglycidyl derivatives 12. Moreover, carboxymethylstarch could be replaced by maleate 13, succinate 14, 15, citraconic 16,

phthalates half esters 17, sulfate 18, sulfonate 19, phosphate starches 20 and cationic starches 21, 22 as well. Other examples are carboxylate acetal 23, citrate 24, acognitate 25, N,N-dicarboxymethylamine 26, N,N,N-tricarboxymethylammonium 27, citrate 28; the last 3 compounds utilising epichlorohydrin as linker arm; and ethylenediamitetraacetate (EDTA) conjugate 29.

5

Examples of starches useful as starting materials are: corn, wheat, rice, potato, tapioca, waxy maize, sorghum, sago, waxy sorghum, physically modified starches and non-gelatinized starches. Other polysaccharides can also be used such as cellulose, gums, dextrines, polygalactomannan, and chitosan. In all cases, anionic and cationic functionalizations of the selected polysaccharide could be introduced before or after the crosslinking

10

#### Water Retention Unit (WRU)

15

The Water Retention Unit (WRU) has been measured by the following procedure.

20

Two empty 15 ml test tubes (duplicata) are weighted ( $T_e$ ). Samples around 0.3g  $\pm$  0.005g (S) are introduced into both tubes. Saline solution (10 ml, 0.9%) is added and the gel is vortexed for 1 minute then allowed to stand for 15 minutes. Tubes are centrifuged at 2000RPM for 5 minutes and the upper aqueous layer is decanted at 30° angle for 5 seconds and tubes are weighted again ( $T_s$ ). In case there is no aqueous layer, the

procedure is repeated with  $0.2g \pm 0.005g$  samples. WRU is calculated according to the equation (1) and is expressed in g of saline solution per g of absorbent.

5

$$\text{WRU} = \frac{\text{Ts-Te-S}}{\text{S}} \quad (1)$$

Those skilled in the art will gain further and better understanding of this invention and the new and important advantages, which is offered from the following illustrative, but not limiting, examples of this invention as it has been carried out.

10

#### EXAMPLE 1

Preparation of the crosslinker 1,5-dichloro-3-oxapentane (dichlorodiethylene oxide 4).

15

10.0g (0.094 mol) of diethylene glycol were dissolved in 100 ml benzene. To this solution, 30.8 ml (4eq.) of pyridine were added, followed by a dropwise addition of 27.5 ml (4eq.) of thionylchloride. The reaction mixture was heated at reflux for 24 hours. At room temperature, the organic layer was decanted from the pyridinium hydrochloride salt, washed with 150 ml of water, dried on anhydrous sodium sulfate, filtered and evaporated to dryness to give 8.4g (65% yield) of the dichloride as a light yellow liquid, used without further purification. Infrared spectroscopy showed the absence of hydroxyl band.

20

IR (neat): 2964, 2865, 1450, 1125, 747, 669  $\text{cm}^{-1}$ .

## 5 EXAMPLE 2

Preparation of the cross-linker 1,8-dichloro-3,6-dioxaoctane (dichlorotriethylene dioxide 5).

10 10.0g (0.067 mol) of triethylene glycol were treated as example 1 with 22 ml (4eq.) of pyridine and 19ml (4eq.) of thionylchloride to give 8.8 g (62% yield) of the dichloride as a yellow oil, used without further purification. Infrared spectroscopy showed the absence of hydroxyl band.

IR (neat): 2962, 2870, 1452, 1123, 747, 666  $\text{cm}^{-1}$ .

15

## EXAMPLE 3

Preparation of the crosslinker 1,11-dichloro-3,6,9-trioxaundecane (dichlorotetraethylene trioxyde 6).

20

10.0g (0.052 mol) of tetraethylene glycol were treated as example 1 with 17 ml (4eq. ) of pyridine and 15 ml (4eq.) of thionylchloride to give 7.2g (61% yield) of the dichloride

as a yellow oil, used without further purification. Infrared spectroscopy showed the absence of hydroxyl band.

IR (neat): 2951, 2870, 1459, 1118, 746, 665 cm<sup>-1</sup>.

5

#### EXAMPLE 4

Preparation of a carboxymethylstarch, crosslinked with divinylsulfone (0.62%), compound 7.

10

2.0g (0.0123 mol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 3.5 ml 30% NaOH (0.0263 mol, 2.1 eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Chloroacetic acid (1.16 g, 0.0123 mol, 1 eq), dissolved in 10 ml of deionized water and neutralized with 1.6 ml 30% NaOH (0.0123 mol, 1 eq.) was added dropwise and the reaction mixture was heated at 70°C for 24 hours. At room temperature, 12mg (0.62 weight %) of divinylsulfone dissolved in 10ml acetone, was added dropwise and the solution was stirred for 2 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60°C for 16 hours to give 1.97g of a white solid. The solid was grinded with a coffee grinder to get a fine powder.

IR (KBr): 3428, 2928, 1611, 1430, 1159, 1083, 1020, 762, 711, 577 cm<sup>-1</sup>.

## EXAMPLE 5

Preparation of a carboxymethylstarch, crosslinked with divinylsulfone (39.38%), compound 7.

5

2.0g (0.0123 mol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 3.5 ml 30% NaOH (0.0263 mol, 2.1 eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Chloroacetic acid (1.16 g, 0.0123 mol, 1 eq), dissolved in 10 ml of deionized water and neutralized with 1.6 ml 30% NaOH (0.0123 mol, 1 eq.) was added dropwise and the reaction mixture was heated at 70°C for 24 hours. At room temperature, 0.784g (39.38% weight %) of divinylsulfone dissolved in 10ml acetone, was added dropwise and the solution was stirred for 2 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60°C for 16 hours to give 2.35g of a white solid. The solid was grinded with a coffee grinder to get a fine powder of compound 7.

15

IR (KBr): , 3427, 2927, 1603, 1415, 1321, 1154, 1083, 1025, 712, 578 cm<sup>-1</sup>.

20

## EXAMPLE 6

Preparation of a starch cicatronic half ester, crosslinked with divinylsulfone (0.62%), compound 9.

2.0g (0.0123 mol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 5.0 ml 30% NaOH (0.0375 mol, 3eq..) was added dropwise and the solution stirred at room temperature for 1 hour. Citraconic anhydride (1.73g, 0.0133 mol, 1.1eq.), dissolved in 10ml acetone was added dropwise and the reaction mixture was stirred at room temperature for 2 hours. 12mg (0.62%) of divinylsulfone, dissolved in 10ml acetone, was added dropwise and the solution was stirred for 2 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60°C for 16 hours to give 1.92g of a white solid. The solid was grinded with a coffee grinder to get a fine powder of compound 9.

IR (KBr): 3399, 2929, 1715, 1644, 1571, 1446, 1407, 1276, 1153, 1081, 1026, 930, 853, 762, 710, 579, 530  $\text{cm}^{-1}$ .

15 EXAMPLE 7

Preparation of carboxymethylstarch, crosslinked with dichlorotriethylene dioxyde (9.85%), compound 8.

20 2.0g (0.0123 mol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 3.5 ml 30% NaOH (0.0263 mol, 2.1eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Chloroacetic acid (1.16 g, 0.0123 mol, 1eq), dissolved in 10 ml of deionized water and neutralized with

1.6 ml 30% NaOH (0.0123 mol, 1 eq.) was added dropwise and the reaction mixture was heated at 70°C for 24 hours. At room temperature, 0.197g (9.85% weight %) of dichlorotriethylene dioxide dissolved in 10ml acetone, was added dropwise and the solution was heated at 70°C for 24 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60°C for 16 hours to give 1.95g of a white solid. The solid was grinded with a coffee grinder to get a fine powder of compound 8.

IR (KBr): 3408, 2929, 1607, 1423, 1327, 1158, 1083, 1021, 937, 849, 762, 710, 581, 530cm<sup>-1</sup>.

## EXAMPLE 8

Preparation of carboxymethylstarch, crosslinked with dichlorotriethylene dioxide (40%), compound 8.

5

2.0g (0.0123 mol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 3.5 ml 30% NaOH (0.0263 mol, 2.1 eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Chloroacetic acid (1.16 g, 0.0123 mol, 1 eq), dissolved in 10 ml of deionized water and neutralized with 1.6 ml 30% NaOH (0.0123 mol, 1 eq.) was added dropwise and the reaction mixture was heated at 70°C for 24 hours. At room temperature, 0.80g (40 weight %) of dichlorotriethylene dioxide dissolved in 10ml acetone, was added dropwise and the solution was heated at 70°C for 24 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60°C for 16 hours to give 2.06g of a white solid. The solid was grinded with a coffee grinder to get a fine powder of compound 8.

10

IR (KBr): 3404, 2928, 1607, 1424, 1327, 1155, 1084, 1020, 934, 849, 762, 710, 580, 530cm<sup>-1</sup>.

15

## 20 REFERENCES

1. Andergen U. and Oppermann W. *Polymer*, 1990, 31, 1854-1858.
2. Kabra WO 95/31500, Nov., 1995
3. Annergren et al. WO 00/21581, Apr., 2000.

**CROSSLINKED POLYSACCHARIDES WITH POLYETHYLENE OXIDES  
AND THEIR USE AS BIODEGRADABLE ABSORBENT MATERIALS**

The present invention relates to new crosslinked polysaccharides useful as  
5 absorbents alone or in a mixture which are obtained by reacting polysaccharides with  
at least one crosslinker selected in the group constituted by halogenated (Cl, Br, I),  
mesylated, tosylated, or triflated polyethylene glycol.

10 The present invention also relates to processes for preparing said crosslinked  
polysaccharides.

The present invention also relates to the use of the crosslinked polysaccharides  
of the invention as superabsorbents, more particularly as inexpensive and/or  
hypoallergenic biodegradable superabsorbents.

15

The invention also relates to superabsorbents mixtures comprising at least one  
of crosslinked polysaccharides of the invention.

**BACKGROUND OF THE INVENTION**

20

Carboxymethylcellulose (CMC) and carboxymethylstarch (CMA) are among known  
polysaccharide-based superabsorbents.

Anbergen and Oppermann<sup>1</sup> have studied the elasticity and the swelling behaviour of sodium carboxymethylcellulose and hydroxyethylcellulose, chemically crosslinked with divinylsulfone 1.

5 In a patent issued in 1995, Kabra<sup>2</sup> reported the sorption capacity of hydroxypropylcellulose, crosslinked with different concentration of divinylsulfone (from 0.28 to 2.98 weight %). His best result showed a water sorption capacity of 44 g/g with a crosslink of 0.91 weight %. The author also mentions that other hydrophobically modified carbohydrate polymers can be chosen, such as  
10 hydroxypropylstarch.

More recently, a patent has been granted to SCA Hygiene Products AB<sup>3</sup> which extends the study with divinylsulfone to low-cost, readily available, renewable starting materials such as carboxymethylcellulose, carboxymethylstarch, and others.  
15 According to the authors, results may be obtained with a mixture of carboxymethylcellulose: hydroxyethylcellulose (3 : 1) which absorbs close to 95 g of synthetic urine per g of polymer after free swelling for 120 min. In this patent, however, the quantity of divinylsulfone used is not reported. The same company has extended their work with divinylsulfone to other polysaccharides containing acidic  
20 groups<sup>4</sup>. It appears that the best result was obtained with carboxymethylcellulose crosslinked with 14 mol% of divinylsulfone. This results in a centrifuge retention capacity (CRC) of 111 g/g with synthetic urine. On page 6 of the patent<sup>4</sup>, it has been

mentioned that the superabsorbent polysaccharides combine high absorption capacity with control of bacterial growth and control of odour, as well as with biodegradability. There is however no evidence that such compounds would be biodegradable, particularly since it is well known that carboxymethylcellulose and 5 carboxymethylstarch are not completely biodegradable. Moreover, it appears to us that the diethylsulfone diether linkage is not biocompatible.

Therefore, there is still a need for new polysaccharide-based superabsorbents with significant biodegradability.

10

Camelot Superabsorbents Limited has reported non polysaccharide-based copolymers having two or more pendant carboxylic acid groups arranged in mutual proximity to absorb water containing multivalent, particularly divalent ions. In more specific examples, monomers having two carboxylic acid groups attached to adjacent carbon 15 atoms are particularly preferred. In this current invention, we report the use of iminodiacetic acid disodium salt and citric acid trisodium salt as dicarboxylates and tricarboxylates pendant anionic groups to chelate divalent ions such as calcium. As a matter of fact, iminodiacetic acid disodium salt have been attached to starch to produce effective materials for heavy metal removal such as copper and cadmium. 20 On the other hand, citric acid also has been attached to starch through its carboxylic acid groups for applications as ion exchanger or to enhance the dietary fibre content in foods. In our invention, we have attached sodium citrate to starch through the

secondary hydroxy group with epichlorohydrin as linker arm, leaving the tricarboxylates groups free, for calcium chelation and water absorption.

#### DESCRIPTION OF THE INVENTION

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The new crosslinked polysaccharides according to the invention are obtained by reacting polysaccharides with at least one activated polyethylene glycol where hydroxy groups are replaced by Cl, Br, I, mesylates, tosylates or triflates.

10 A preferred embodiment of the invention is constituted by crosslinking starches with at least one activated polyethylene glycol. As a matter of exemplification, starches crosslinked with dichloropolyethylene oxide are preferred particularly since starch is a renewable and inexpensive starting material and some dichloropolyethylene oxide are commercially available or easily prepared from 15 polyethylene glycols by reaction at reflux with thionyl chloride in benzene or dichloromethane in the presence of pyridine.

20 The crosslinked starches according to the invention are characterized by alkylation on primaries hydroxyl groups of the polymeric unit, then on secondaries hydroxyl groups at C2 or C3 carbon atoms of the polysaccharide.

Crosslinkers used to prepare crosslinked starches of the invention are activated

polyethylene glycols with average molecular weight varying from 100 to 10,000 and preferably from 100 to 300.

5 Polyethylene glycol (PEG 2,) has been used in blended starches for specific applications<sup>5-9</sup>. Starch can react with ethylene glycol in the presence of an acid catalyst at elevated temperature to yield crude mixtures of glycol glucosides by cleavage of glycosidic bonds<sup>10,11</sup>. By high energy radiation, it is possible to link poly(ethylene oxide) to starch<sup>12</sup>. It has also been reported that starch dialdehyde reacts with polyethylene glycol to give an acetal functionality<sup>13</sup>; Ethylene oxide can 10 be grafted to starch by anionic polymerization<sup>14,15</sup> and polyethylene glycol chloroformate derivative<sup>16</sup> or ethylene glycol chloroformate<sup>17</sup> can also be used to crosslink starch. Moreover, diglycidyl ether<sup>18</sup>, polyglycidyl ethers<sup>19</sup> and ethylene glycol dimethacrylate<sup>20</sup> are among known crosslinkers.

15 Polyethylene glycols are biodegradable aerobically and anaerobically<sup>21</sup> and the microbial oxidation of diethylene glycol and polyethylene glycol with the average molecular weights of 200, 400, 600, 1000 and 2000 have been reported<sup>22</sup>.

According to the Zahn-Wellens/EMPA test <sup>ref</sup>, starch A maleate half-ester, 20 crosslinked with triglycol dichloride 5 which has a CRC of 30g/g in saline solution (example 21 ), showed 77,3%, 92,3% and 96,1% biodegradability after respectively 14, 28 and 46 days. The study of the crosslinker length was performed by preparing

di 4, tri 5 and tetra glycol dichloride 6 ( $\text{SOCl}_2$ , pyridine, dichloromethane or benzene, reflux). Experimental results thereby obtained show that carboxymethylstarch crosslinked with 0.62% of divinylsulfone 7, gives a CRC of 23 g/g in 0.9% saline solution, compared to 30 g/g when crosslinked with 9.85% of triglycol dichloride 8.

5 The starch-citraconic half ester crosslinked with 0.6% of divinylsulfone 9 were found to exhibit a good CRC (25 g/g), suggesting that carboxymethyl groups could be replaced by half esters. The effect of divinylsulfone and dichlorotriethylene dioxide concentrations on the water retention of crosslinked carboxymethylstarch in 0.9% saline solution, are shown on figures 1 and 2. Even if 15 times more quantity of  
10 dichlorotriethylene dioxide is required to reach the maximum water retention, the choice of the former is still advantageous since divinylsulfone is very expensive.

15 Crosslinked carboxymethylstarches with activated polyethylene glycols (figure 1) can be prepared in two steps. First, starch can be alkylated with sodium chloroacetate followed by crosslinkage with activated polyethylene glycols. In reverse order, it is possible to perform the crosslinkage before the alkylation step without negative effect on the water retention. Furthermore, these crosslinked carboxymethylstarches can also be prepared in one pot, without affecting the water retention.

20

Other known activated polyethylene glycols may be used as crosslinkers. For instance, dichloroformates derivatives 10; and diglycidyl derivatives 12. Moreover,

carboxyalkylstarch could be replaced by maleate 13, succinate 14, 15, citraconic 16, and phthalates half esters 17, as well. These starch half esters alone, without crosslinkage have been reported to be biodegradable detergent builders and biodegradable non-aging superabsorbers.

5

Examples of starches useful as starting materials are: corn, wheat, rice, potato, tapioca, waxy maize, sorghum, sago, waxy sorghum, and physically modified starches. Other polysaccharides can also be used such as cellulose, gums, dextrans, polygalactomannan, chitosan and pectin. In all cases, anionic and cationic 10 functionalizations of the selected polysaccharide could be introduced before, during and after the crosslinkage.

For the attachment of iminodicarboxylic acid disodium salt and citric acid trisodium salt to starch, we choose epichlorohydrin as linker arm. Epichlorohydrin have been 15 used as crosslinker for carboxymethylstarch to obtain absorbent materials. Moreover, this linker arm showed application to attach primary, secondary and tertiary amines and we have adapted the procedure for the attachment of the secondary alcohol of sodium citrate. In practice, epichlorohydrin can be attach first to starch with acid catalyst, followed by amination with iminodiacetic acid disodium salt or o-alkylation of 20 sodium citrate in basic conditions. However, it has been reported that starch and epichlorohydrin appeared to form unstable adducts when hydrochloric acid catalysis was used. Since perchloric acid is a better catalyst than hydrochloric acid to give

higher incorporation rate of epichlorohydrin on starch, and since perchloric acid is explosive, we choose an alternative approach. Therefore, since epichlorohydrin-  
5 tertiary amines adducts can be prepared first in basic condition, followed by attachment to starch in basic condition we have selected this alternative procedure for the attachment of iminodiacetic acid disodium salt and sodium citrate on starch.

For comparaison, we have tested diglycidyl ethers as alternative crosslinker for activated polyethylene glycol. Ethylene glycol diglycidyl ether is preferred and this crosslinker possesses structural similarities with triethylene glycol in regard to the  
10 polyethyle oxide backbone.

#### **Centrifuge Retention Capacity (CRC)**

The centrifuge retention capacity (CRC) has been measured by the following  
15 procedure which represents a modified procedure from the EDANA test method and a modified procedure described by Annengren and Lundstrom.

Two empty 15 ml test tubes (duplicata) are weighted ( $T_e$ ). Samples around  $0.3\text{g} \pm 0.005\text{g}$  ( $S$ ) are introduced into both tubes. Saline solution (0.9%, 10 ml) is added and  
20 the gel is vortexed for 1 minute then allowed to stand for 15 minutes. Tubes are centrifuged at 2000RPM for 5 minutes and the upper aqueous layer is decanted at  $30^\circ$  angle for 5 seconds and tubes are weighted again ( $T_s$ ). In case there is no aqueous

layer, the procedure is repeated with  $0.2g \pm 0.005g$  samples. CRC is calculated according to the equation (1) and is expressed in g of saline solution per g of absorbent.

5

$$\text{CRC} = \frac{\text{Ts-Te-S}}{\text{S}} \quad (1)$$

10

Those skilled in the art will gain further and better understanding of this invention and the new and important advantages, which is offered from the following illustrative, but not limiting, examples of this invention as it has been carried out.

### Gel Strength

15

The gel strength is arbitrary measured on a 0 to 5 scale, where 0 = no gel, 1 = viscous liquid, 2 = weak gel, 3 = medium gel, 4 = strong gel and 5 = very strong gel

### Biodegradability

20

According to the United States Environmental Protection Agency (EPA), the Zahn-Wellens test is useful to test the biodegradability of a substance soluble in water to at least 50 mg of dissolved organic carbon DOC per litre<sup>ref</sup>. For substances which are not completely soluble it offers only a qualitative indication of whether these substances are basically susceptible to biological degradation or not<sup>Buchholz et al</sup>.

*Preparation of crosslinkers*

## EXAMPLE 1

5 Preparation of the 1,5-dichloro-3-oxapentane (diglycol dichloride **4**).

10.0g (94 mmol) of diethylene glycol were dissolved in 100 ml benzene. To this solution, 30.8 ml (4eq.) of pyridine were added, followed by a dropwise addition of 27.5 ml (4eq.) of thionylchloride. The reaction mixture was heated at reflux for 24 hours. At room temperature, the organic layer was decanted from the pyridinium hydrochloride salt, washed with 150 ml of water, dried on anhydrous sodium sulfate, filtered and evaporated to dryness to give 8.4g (65% yield) of the dichloride as a light yellow liquid, used without further purification. Infrared spectroscopy showed the absence of hydroxyl band.

15 IR (neat): 2964, 2865, 1450, 1125, 747, 669  $\text{cm}^{-1}$ .

## EXAMPLE 2

Preparation of 1,8-dichloro-3,6-dioxaoctane (triglycol dichloride **5**).

20

10.0g (67 mmol) of triethylene glycol were treated as example 1 with 22 ml (4eq.) of pyridine and 19ml (4eq.) of thionylchloride to give 8.8 g (62% yield) of the dichloride

as a yellow oil, used without further purification. Infrared spectroscopy showed the absence of hydroxyl band.

IR (neat): 2962, 2870, 1452, 1123, 747, 666 cm<sup>-1</sup>.

5 EXAMPLE 3

Preparation of 1,11-dichloro-3,6,9-trioxaundecane  
(tetraglycol dichloride 6).

10 10.0g (52 mmol) of tetraethylene glycol were treated as example 1 with 17 ml (4eq.) of pyridine and 15 ml (4eq.) of thionylchloride to give 7.2g (61% yield) of the dichloride as a yellow oil, used without further purification. Infrared spectroscopy showed the absence of hydroxyl band.

IR (neat): 2951, 2870, 1459, 1118, 746, 665 cm<sup>-1</sup>.

15

*Comparaison of Divinylsulfone and triglycol dichloride as crosslinkers to obtain starch-based superabsorbents (figures 1,2)*

EXAMPLE 4

20 Preparation of a carboxymethylstarch, crosslinked with 0.62% w/w divinylsulfone, compound 7 (figure 1).

2.0g (12.3 mmol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 3.5 ml 30% NaOH (26.3 mmol, 2.1eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Chloroacetic acid (1.16 g, 12.3 mmol, 1eq), dissolved in 10 ml of deionized water and neutralized with 1.6 ml 30% NaOH (12.3 mmol, 1 eq.) was added dropwise and the reaction mixture was heated at 70<sup>0</sup>C for 24 hours. At room temperature, 12mg (0.62 weight %) of divinylsulfone dissolved in 10ml acetone, was added dropwise and the solution was stirred for 2 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60<sup>0</sup>C for 16 hours to give 1.97g of a white solid. The solid was grinded with a coffee grinder to get a fine powder.

IR (KBr): 3428, 2928, 1611, 1430, 1159, 1083, 1020, 762, 711, 577 cm<sup>-1</sup>.

CRC = 23 g/g

15 EXAMPLE 5

Preparation of a carboxymethylstarch, crosslinked with 39.38% w/w divinylsulfone, compound 7 (figure 1).

20 2.0g of wheat starch A was treated as in example 4 with 0.784g (39.38% weight %) of divinylsulfone dissolved in 10ml acetone to give 2.35g of compound 7 as a fine white powder.

IR (KBr): , 3427, 2927, 1603, 1415, 1321, 1154, 1083, 1025, 712, 578  $\text{cm}^{-1}$ .

CRC = 5.7 g/g

Examples 5, 7 and other are shown in table I

5

#### EXAMPLE 6

Preparation of carboxymethylstarch, crosslinked with 9.85% w/w triglycol dichloride, compound 8 (figure 1).

10

2.0g (12.3 mmol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring, 3.5 ml 30% NaOH (26.3 mmol, 2.1eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Chloroacetic acid (1.16 g, 12.3 mmol, 1.0eq), dissolved in 10 ml of deionized water and neutralized with 1.6 ml 30% NaOH (12.3 mmol, 1.0eq.) was added dropwise and the reaction mixture was heated at 70°C for 24 hours. At room temperature, 0.197g (9.85% weight %) of triglycol dichloride dissolved in 10ml acetone, was added dropwise and the solution was heated at 70°C for 24 hours. The polymer was precipitated with 100 ml of methanol, triturated in a blender, washed with 3 portions of 60 ml methanol, filtered and dry at 60°C for 16 hours to give 1.95g of a white solid. The solid was grinded with a coffee grinder to get a fine powder of compound 8.

15

20

36

IR (KBr): 3408, 2929, 1607, 1423, 1327, 1158, 1083, 1021, 937, 849, 762, 710, 581, 530cm<sup>-1</sup>.

CRC = 0 g/g

5 EXAMPLE 7

Preparation of carboxymethylstarch, crosslinked with 40% w/w triglycol dichloride, compound 8 (figure 1).

10 2.0g of wheat starch A was treated as in example 7 with 0.80g (40 weight %) of triglycol dichloride dissolved in 10ml acetone to give 2.06g of compound 8 as a fine white powder.

IR (KBr): 3404, 2928, 1607, 1424, 1327, 1155, 1084, 1020, 934, 849, 762, 710, 580, 530cm<sup>-1</sup>.

15 CRC = 21 g/g

Examples 6, 7 and other are shown in table II

*Effect of sodium chloroacetate concentration, crosslinker length and crosslinker**Concentration on CRC*

## EXAMPLE 8

5 Preparation of carboxymethylstarch, with 0,25eq sodium chloroacetate and without crosslinkage, compound X (figure 2).

2.0g (12.3 mol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring at 2000 rpm, 5.0 ml 30% NaOH (37mmol, 10 3.0eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Sodium chloroacetate (1.13ml, 2.74M, 3.10 mmol, 0.25eq) was added dropwise and the reaction mixture was heated at 70°C for 16 hours. The polymer was precipitated with 75 ml of methanol, and the mother liquor is discarded. The polymer is triturated in a blender with 150ml methanol, filtered, washed with 3 portions of 50 ml methanol, 15 and dry at 60°C for 16 hours to give compound 8 as a fine white powder after grinding.

CRC = 1g/g

Gel Strength = 0

## EXAMPLE 9

Preparation of carboxymethylstarch with 2.0eq. sodium chloroacetate and crosslinked with 0.05eq. diglycol dichloride, compound (figure 2)

5

2.0g (12.3 mmol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 40 ml of deionized water. Under stirring at 2000 rpm, 5.0 ml 30% NaOH (37mmol, 3.0eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Sodium chloroacetate (9.0ml, 2.74M, 24.7mmol, 2.0eq) was 10 added dropwise followed by diglycol dichloride (88mg, 6.17mmol, 0.05eq.), weighted in 1.0 ml seringue, and the reaction mixture was heated at 70°C for 16 hours. The polymer was treated as in example 9 to give a fine powder of compound 8.

CRC = 52g/g

Gel strength = 2

15

## EXAMPLE 10

Preparation of carboxymethylstarch with 0.5eq. sodium chloroacetate and crosslinked with 0.20eq. diglycol dichloride, compound (figure 2)

20

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (2.26ml, 2.74M, 6.17 mmol, 0.5eq) and diglycol dichloride (353mg,

2.47 mmol, 0.20eq.) to give a fine powder of compound 8.

CRC = 11g/g

Gel strength = 4

5 EXAMPLE 11

Preparation of carboxymethylstarch with 2.0eq. sodium chloroacetate and crosslinked with 0.20eq. diglycol dichloride, compound (figure 2)

10 2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (9.0ml, 2.74M, 24.7 mmol, 2.0eq.) and diglycol dichloride (353mg, 2.47 mmol, 0.20eq.) to give a fine powder of compound 8.

CRC = 33g/g

Gel strength = 4

15

Examples 8 to 11 and other are shown in table III

EXAMPLE 12

20 Preparation of carboxymethylstarch with 0.5eq. sodium chloroacetate and crosslinked with 0.05eq. triglycol dichloride, compound (figure 3)

40

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (2.3ml, 2.74M, 6.17 mmol, 0.5eq.) and triglycolglycol dichloride (115mg, 0.62 mmol, 0.05eq.) to give a fine powder of compound 8.

CRC = 11g/g

5 Gel strength = 2

#### EXAMPLE 13

10 Preparation of carboxymethylstarch with 2.0eq. sodium chloroacetate and crosslinked with 0.10eq. triglycol dichloride, compound (figure 3)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (9.0ml, 2.74M, 24.7 mmol, 2.0eq.) and triglycolglycol dichloride (115mg, 0.062 mmol, 0.05eq.) to give a fine powder of compound 8.

15 CRC = 49g/g

Gel strength = 3

#### EXAMPLE 14

20 Preparation of carboxymethylstarch with 1.5eq. sodium chloroacetate and crosslinked with 0.15eq. triglycol dichloride, compound (figure 3)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (6.8ml, 2.74M, 18.5 mmol, 1.5eq.) and triglycolglycol dichloride (346mg, 1.85 mmol, 0.15eq.) to give a fine powder of compound 8.

CRC = 27g/g

5 Gel strength = 5

#### EXAMPLE 15

Preparation of carboxymethylstarch with 0.25eq. sodium chloroacetate and  
10 crosslinked with 0.20eq. triglycol dichloride, compound (figure 3)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (1.1ml, 2.74M, 3.09 mmol, 0.25eq.) and triglycolglycol dichloride (462mg, 2.47 mmol, 0.20eq.) to give a fine powder of compound 8.

15 CRC = 15g/g

Gel strength = 2

Examples 12 to 15 and other are shown in table IV

20 EXAMPLE 16

Preparation of carboxymethylstarch with 0.50eq. sodium chloroacetate and

42

crosslinked with 0.05eq. tetraglycol dichloride, compound (figure 4)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (2.3ml, 2.74M, 6.17 mmol, 0.50eq.) and tetraglycolglycol dichloride (143mg, 0.617 mmol, 0.05eq.) to give a fine powder of compound 8.

5 CRC = 17g/g

Gel strength = 5

#### EXAMPLE 17

10

Preparation of carboxymethylstarch with 2.0eq. sodium chloroacetate and crosslinked with 0.05eq. tetraglycol dichloride, compound 8 (figure 4)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (9.0ml, 2.74M, 24.7 mmol, 2.0eq.) and tetraglycolglycol dichloride (143mg, 0.617 mmol, 0.05eq.) to give a fine powder of compound 8.

15 CRC = 33g/g

Gel strength = 5

20

#### EXAMPLE 18

Preparation of carboxymethylstarch with 1.0eq. sodium chloroacetate and crosslinked

43

with 0.15eq. tetraglycol dichloride, compound 8 (figure 4)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 with sodium chloroacetate (4.5ml, 2.74M, 12.3 mmol, 1.0eq.) and tetraglycolglycol dichloride (428mg, 1.85 mmol, 0.15eq.) to give a fine powder of compound 9.

5 CRC = 25g/g

Gel strength = 3

#### EXAMPLE 19

10

Preparation of starch crosslinked with 0.25eq. tetraglycol dichloride, compound 8 (figure 4)

2.0g (12.3 mmol) of wheat starch A was treated as in example 10 except that sodium 15 chloroacetate was omitted and tetraglycol dichloride (713mg, 3.09 mmol, 0.25eq.) was used to give a fine powder of compound 8.

CRC = 17g/g

Gel strength = 3

20

Examples 16 to 19 and other appear in table V

*Other carboxylate groups*

## EXAMPLE 20

5 Preparation of starch citraconate half ester, crosslinked with 0.62% w/w  
divinylsulfone compound 9.

10 2.0g (12.3 mmol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was  
suspended in 40 ml of deionized water. Under stirring, 5.0 ml 30% NaOH (37.5  
mmol, 3eq.) was added dropwise and the solution stirred at room temperature for 1  
hour. Citraconic anhydride (1.73g, 13.3 mmol, 1.1eq.), dissolved in 10ml acetone was  
added dropwise and the reaction mixture was stirred at room temperature for 2 hours.  
12mg (0.62%) of divinylsulfone, dissolved in 10ml acetone, was added dropwise and  
the solution was stirred for 2 hours. The polymer was treated as in example 4 to give  
15 1.92g of compound 9 as a fine white powder.

IR (KBr): 3399, 2929, 1715, 1644, 1571, 1446, 1407, 1276, 1153, 1081, 1026, 930,  
853, 762, 710, 579, 530  $\text{cm}^{-1}$ .

CRC = 25g/g

Gel strength = 5

## EXAMPLE 21

Preparation of starch maleate half ester, crosslinked with 0.08eq. triglycol dichloride compound 2.

5

6.0g (37.1 mmol) of wheat starch A ( Supercell 1201-C, ADM/Ogilvie) was suspended in 120 ml of deionized water. Under stirring, 2.5 ml 30% NaOH (18.6 mmol, 0.5eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Triglycol dichloride (0.5 ml, 2.97 mmol, 0.08eq.) was added and the solution 10 was heated at 70°C for 16 hours. After cooling at room temperature, maleic anhydride (18ml, 1.64M in ethyl acetate, 29.6 mmol, 0.8eq.) was added and the two phases mixture was vigorously stirred at room temperature for 1 hour. The polymer was precipitated with 225 ml of methanol, and the mother liquor is discarded. The polymer is triturated in a blender with 450 ml methanol, filtered, washed with 3 15 portions of 150 ml methanol, and dry at 60°C for 16 hours to give 6.58g of compound 8 as a fine white powder after grinding.

IR (KBr): 3398, 2931, 1720, 1632, 1583, 1423, 1351, 1304, 1228, 1155, 1081, 1024, 934, 850, 762, 709, 610, 578, 530  $\text{cm}^{-1}$ .

CRC = 33g/g

20 Gel strength = 5

Biodegradability: 77.3, 92.3 and 96.1% after 14, 28 and 46 days, respectively.

**46****EXAMPLE 22****Preparation of disodium iminodicarboxylate epichlorohydrin adduct.**

5      Iminodiacetic acid (3.28g, 24.6 mmol) was dissolved in 6.6 ml 30% NaOH (2.0eq.) and epichlorohydrin (1.92 ml, 24.6 mmol) was added. The heterogeneous reaction mixture was stirred at room temperature for 2 hours to give an homogeneous solution which was completed to 20 ml with deionized water. Samples of this stock solution were used without further purification.

10

**EXAMPLE 23****Preparation of trisodium citrate epichlorohydrin adduct**

15     Trisodium citrate (7.23g, 24.6 mmol) was dissolved in 3.3 ml 30% NaOH (1.0eq.) and epichlorohydrin (1.92 ml, 24.6 mmol) was added. The heterogeneous reaction mixture was stirred at room temperature for 16 hours to give an homogeneous solution which was completed to 20 ml with deionized water. Samples of this stock solution were used without further purification.

20

## EXAMPLE 24

## Preparation of starch dicarboxylates

5 2.0g (12.3 mmol) of wheat starch A was suspended in 40 ml of deionized water. Under stirring, 3.3 ml 30% NaOH (24.3 mmol, 2.0eq.) was added dropwise and the solution stirred at room temperature for 1 hour. The disodium iminodiacetate epichlorohydrin adduct solution (15.0 ml 18.45 mmol, 1.5eq), was added dropwise, followed by triglycol dichloride (0.30 ml, 1.85 mmol, 0.15eq.) and the reaction  
10 mixture was heated at 70°C for 24 hours. The polymer was treated as in example 9 to get a fine powder of compound 10.

IR (KBr): 3408, 2929, 1607, 1423, 1327, 1158, 1083, 1021, 937, 849, 762, 710, 581,  
530cm<sup>-1</sup>.

CRC = 24 g/g

15 Gel strength = 4

## EXAMPLE 25

## 20 Preparation of starch tricarboxylates

2.0g (12.3 mmol) of wheat starch A was suspended in 40 ml of deionized water.

## 48

Under stirring, 3.3 ml 30% NaOH (24.3 mmol, 2.0eq.) was added dropwise and the solution stirred at room temperature for 1 hour. The trisodium citrate epichlorohydrin adduct solution (15.0 ml 18.45 mmol, 1.5eq), was added dropwise, followed by triglycol dichloride (0.30 ml, 1.85 mmol, 0.15eq.) and the reaction mixture was heated 5 at 70°C for 24 hours. The polymer was treated as in example 9 to get a fine powder of compound 11.

IR (KBr): 3408, 2929, 1607, 1423, 1327, 1158, 1083, 1021, 937, 849, 762, 710, 581, 530cm<sup>-1</sup>.

CRC = 23 g/g

10 Gel strength = 4

## EXAMPLE 26

15 Preparation of carboxymethylstarch crosslinked with 0.05eq. diethyleneglycol  
diglycidyl ether

2.0g (12.3 mmol) of wheat starch A was suspended in 40 ml of deionized water. Under stirring, 2.5 ml 30% NaOH (18.45mmol, 1.5eq.) was added dropwise and the solution stirred at room temperature for 1 hour. Sodium chloroacetate (6.7 ml, 2.74M, 20 24.7mmol, 1.5eq) was added dropwise followed by diethyleneglycol diglycidyl ether (0.19 ml, 0.05eq., 50% purity). The reaction mixture was heated at 70°C for 16 hours. The polymer was treated as in example 9 to give a fine powder of compound 12.

49

IR (KBr): 3408, 2929, 1607, 1423, 1327, 1158, 1083, 1021, 937, 849, 762, 710, 581, 530cm<sup>-1</sup>.

CRC = 21 g/g

5 EXAMPLE 27

Preparation of carboxymethylstarch crosslinked with 0.10eq. triethyleneglycol diglycidyl ether

10 2.0g (12.3 mmol) of wheat starch A was treated as in example 26 with diethyleneglycol diglycidyl ether (0.38 ml, 0.10eq., 50% purity) to give a fine powder of compound 12.

CRC = 29 g/g

15 EXAMPLE 28

Preparation of carboxymethylstarch crosslinked with 0.20eq. triethyleneglycol diglycidyl ether

20 2.0g (12.3 mmol) of wheat starch A was treated as in example 26 with diethyleneglycol diglycidyl ether (0.77 ml, 0.20eq., 50% purity) to give a fine powder of compound 12.

CRC = 27 g/g

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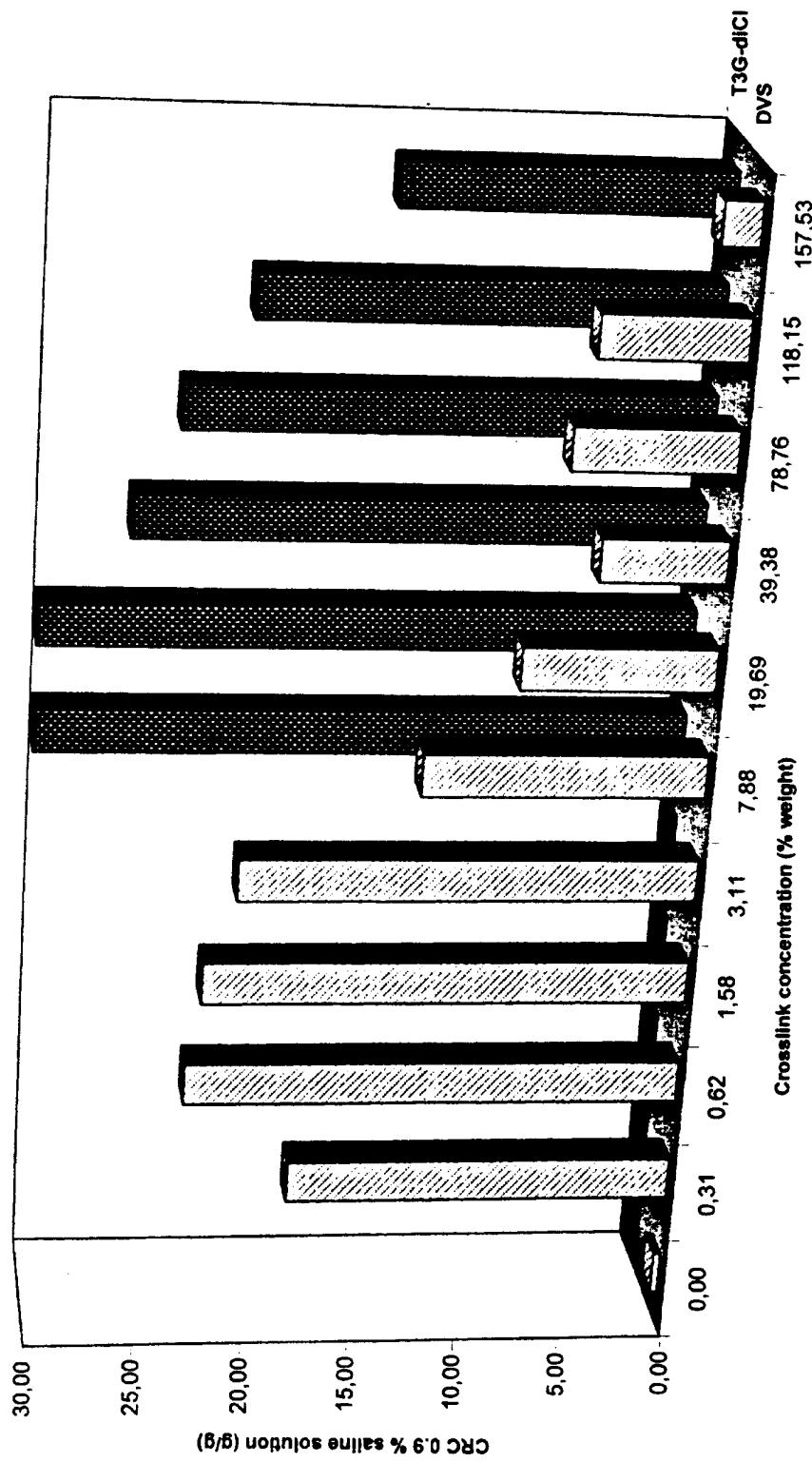
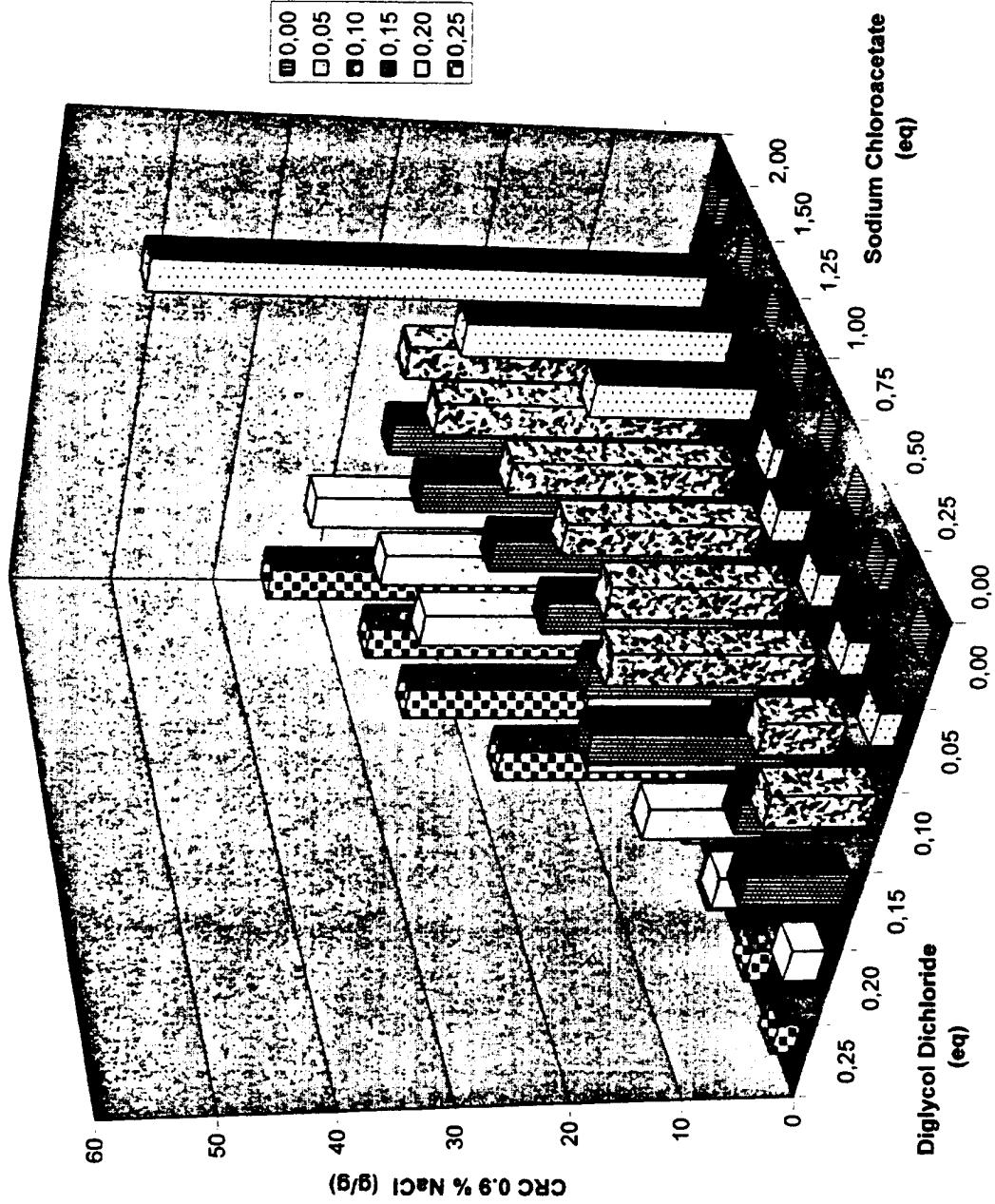
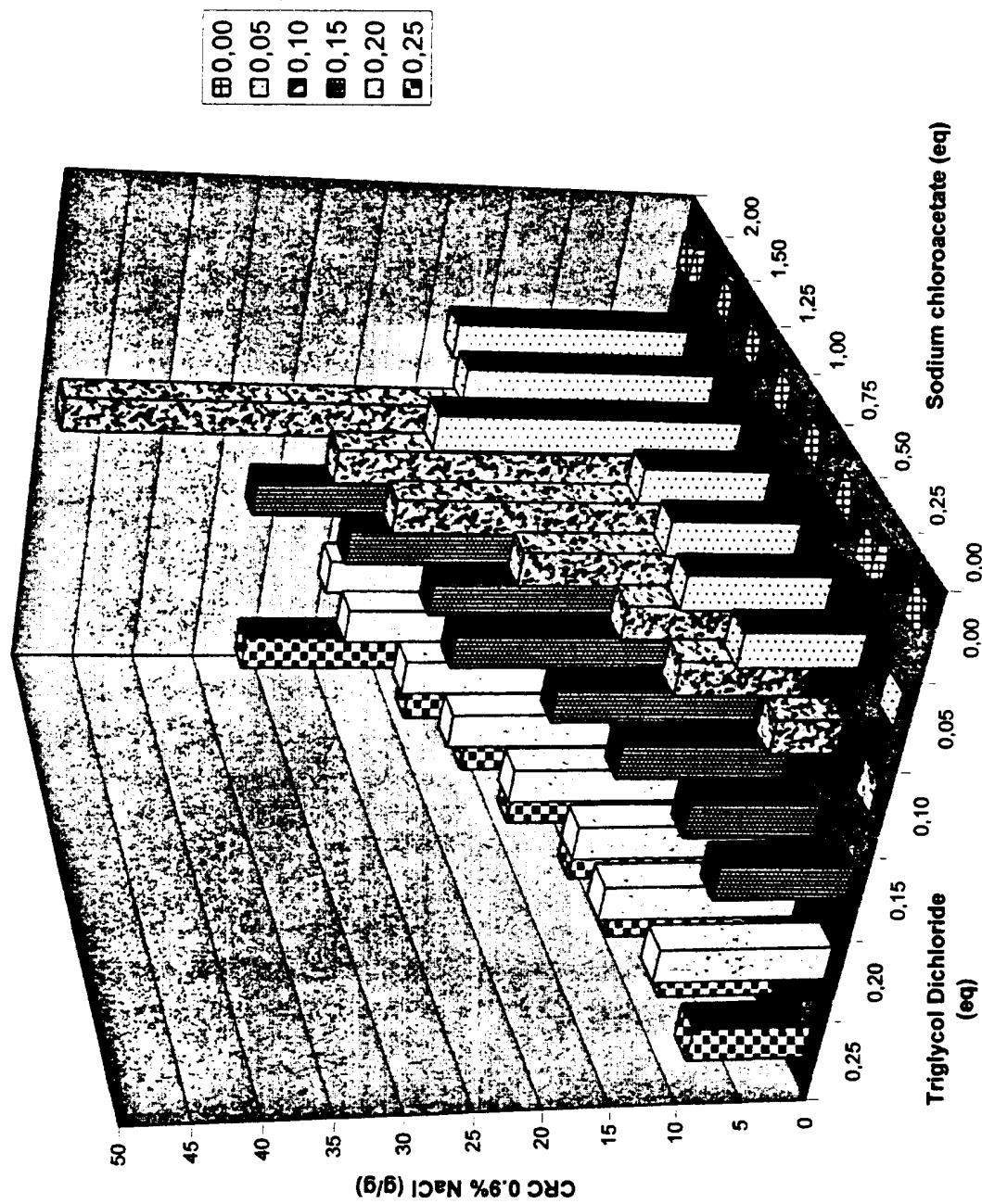
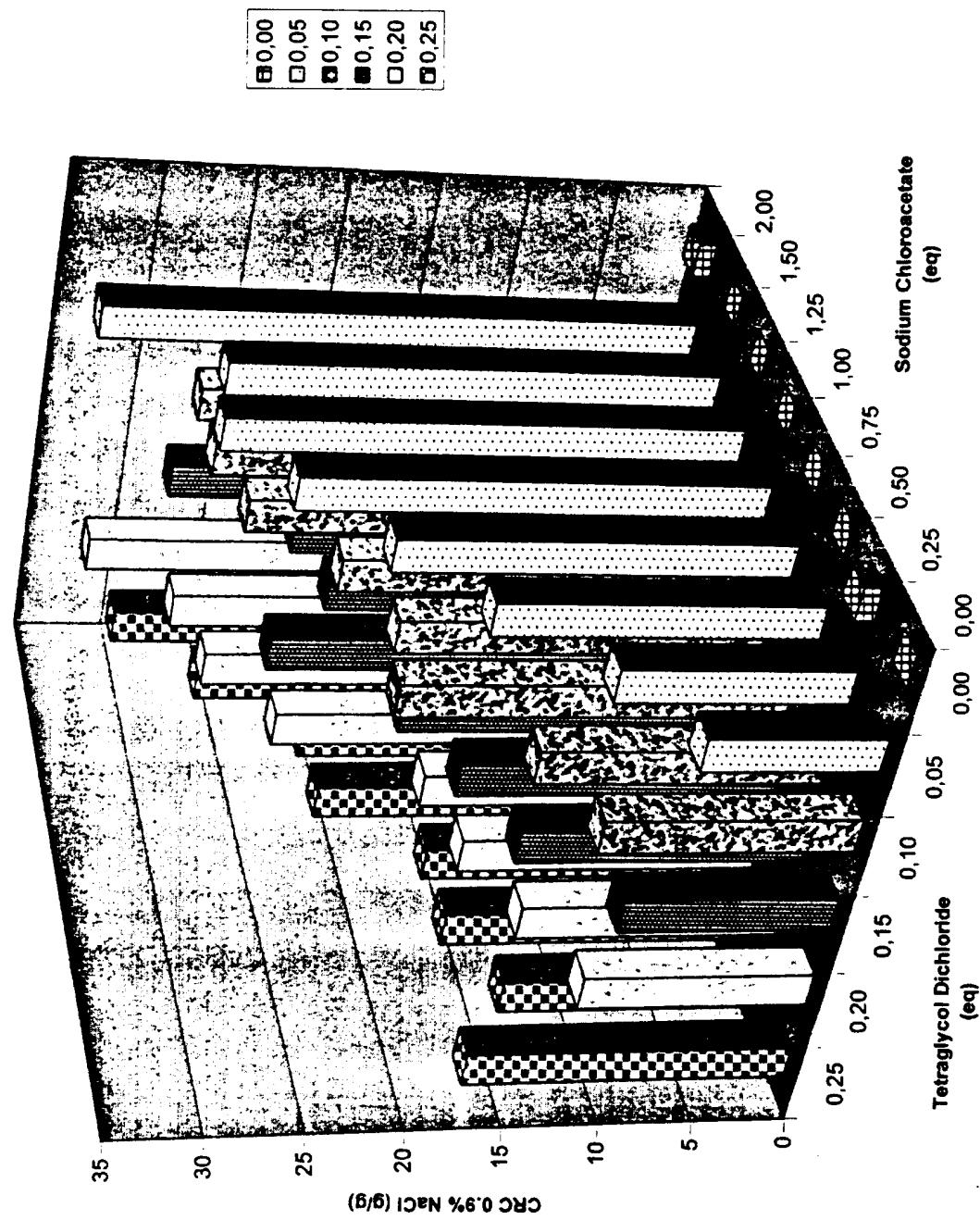


Figure 1 : Effect of triglycol dichloride (T<sub>3</sub>G-diCl) and divinyl sulfone (DVS) concentrations on crosslinked carboxymethylstarch' CRC.







## 57

**Table I**  
 Effect of Divinyl Sulfone (DVS) Concentration on  
 Crosslinked Carboxymethylstarch' CRC.

DVS % w/w	0.00	0.31	0.62	1.58	3.11	7.88	19.69	39.38	78.76	118.15	157.53
CRC (g/g)	0.30	18.00	23.00	22.40	21.00	13.00	8.90	5.70	7.40	6.60	1.70

**Table II**  
 Effect of Triglycol Dichloride (T<sub>3</sub>G-diCl) Concentration on  
 Crosslinked Carboxymethylstarch' CRC.

T <sub>3</sub> GdiCl % w/w	0.00	0.49	0.98	2.46	5.00	9.85	20.00	24.62	30.00	40.00	150.0
CRC (g/g)	0.00	0.00	0.00	0.00	0.00	30.00	30.00	26.00	24.00	21.00	15.00

**Table III**  
**Effect of Sodium Chloroacetate (SCA) and Diglycol Dichloride (DG-diCl)**  
**Concentrations on Starch Derivatives' CRC and Gel Strength (GS).**

SCA (eq)	DG-diCl (eq)	CRC (g/g)	GS (0-5)
0.00	0.00	0	0
0.25	0.00	1	0
0.50	0.00	0	0
0.75	0.00	0	0
1.00	0.00	0	0
1.25	0.00	0	0
1.50	0.00	0	0
2.00	0.00	1	0
0.00	0.05	2	0
0.25	0.05	2	0
0.50	0.05	2	0
0.75	0.05	3	0
1.00	0.05	1	0
1.25	0.05	15	2
1.50	0.05	25	2
2.00	0.05	52	2
0.00	0.10	2	1
0.25	0.10	4	1
0.50	0.10	12	4
0.75	0.10	11	4
1.00	0.10	9	4
1.25	0.10	26	3
1.50	0.10	30	3
2.00	0.10	31	3

SCA (eq)	DG-diCl (eq)	CRC (g/g)	GS (0-5)
0.00	0.15	9	1
0.25	0.15	7	2
0.50	0.15	18	5
0.75	0.15	16	4
1.00	0.15	18	3
1.25	0.15	21	3
1.50	0.15	26	3
2.00	0.15	27	3
0.00	0.20	3	4
0.25	0.20	7	4
0.50	0.20	11	4
0.75	0.20	14	4
1.00	0.20	12	4
1.25	0.20	26	4
1.50	0.20	28	4
2.00	0.20	33	4
0.00	0.25	2	3
0.25	0.25	2	3
0.50	0.25	3	3
0.75	0.25	3	3
1.00	0.25	19	3
1.25	0.25	26	4
1.50	0.25	28	5
2.00	0.25	36	5

**Table IV**  
 Effect of Sodium Chloroacetate (SCA) and Triglycol Dichloride ( $T_3G$ -diCl)  
 Concentrations on Starch Derivatives' CRC and Gel Strength (GS).

SCA (eq)	$T_3G$ diCl (eq)	CRC (g/g)	GS (0-5)
0.00	0.00	0	0
0.25	0.00	1	0
0.50	0.00	0	0
0.75	0.00	0	0
1.00	0.00	0	0
1.25	0.00	0	0
1.50	0.00	0	0
2.00	0.00	1	0
0.00	0.05	0	0
0.25	0.05	9	2
0.50	0.05	11	2
0.75	0.05	10	2
1.00	0.05	10	2
1.25	0.05	24	3
1.50	0.05	20	4
2.00	0.05	19	3
0.00	0.10	0	0
0.25	0.10	5	1
0.50	0.10	10	4
0.75	0.10	12	4
1.00	0.10	18	4
1.25	0.10	26	4
1.50	0.10	29	4
2.00	0.10	49	3

SCA (eq)	$T_3G$ diCl (eq)	CRC (g/g)	GS (0-5)
0.00	0.15	10	4
0.25	0.15	10	2
0.50	0.15	13	3
0.75	0.15	16	4
1.00	0.15	22	5
1.25	0.15	22	5
1.50	0.15	27	5
2.00	0.15	33	4
0.00	0.20	13	2
0.25	0.20	15	2
0.50	0.20	15	4
0.75	0.20	18	4
1.00	0.20	21	4
1.25	0.20	23	4
1.50	0.20	26	4
2.00	0.20	26	5
0.00	0.25	9	3
0.25	0.25	9	3
0.50	0.25	11	3
0.75	0.25	12	4
1.00	0.25	15	4
1.25	0.25	17	4
1.50	0.25	20	4
2.00	0.25	32	3

Table V

Effect of Sodium Chloroacetate (SCA) and Tetraglycol Dichloride ( $T_4G$ -diCl) Concentrations on Starch Derivatives' CRC and Gel Strength (GS).

SCA (eq)	$T_4G$ diCl (eq)	CRC (g/g)	GS (0-5)
0.00	0.00	0	0
0.25	0.00	1	0
0.50	0.00	0	0
0.75	0.00	0	0
1.00	0.00	0	0
1.25	0.00	0	0
1.50	0.00	0	0
2.00	0.00	1	0
0.00	0.05	9	2
0.25	0.05	12	5
0.50	0.05	17	5
0.75	0.05	21	5
1.00	0.05	25	5
1.25	0.05	28	5
1.50	0.05	27	5
2.00	0.05	33	5
0.00	0.10	13	2
0.25	0.10	15	2
0.50	0.10	21	2
0.75	0.10	20	5
1.00	0.10	22	5
1.25	0.10	26	5
1.50	0.10	27	5
2.00	0.10	27	5

SCA (eq)	$T_4G$ diCl (eq)	CRC (g/g)	GS (0-5)
0.00	0.15	11	2
0.25	0.15	15	2
0.50	0.15	17	3
0.75	0.15	19	3
1.00	0.15	25	3
1.25	0.15	21	5
1.50	0.15	22	5
2.00	0.15	28	4
0.00	0.20	12	2
0.25	0.20	14	2
0.50	0.20	16	2
0.75	0.20	17	3
1.00	0.20	24	3
1.25	0.20	27	4
1.50	0.20	28	4
2.00	0.20	32	4
0.00	0.25	17	3
0.25	0.25	14	5
0.50	0.25	16	2
0.75	0.25	16	4
1.00	0.25	21	4
1.25	0.25	21	4
1.50	0.25	26	5
2.00	0.25	30	5

**Claims:**

5

1. Crosslinked polysaccharide (starch) obtained from polysaccharide (starch) by crosslinking with at least one crosslinker selected in the group constituted by activated (preferably halogeno substituted) polyethylene glycols.

10

2. Polysaccharide (starch) crosslinked with a dichloropolyethylene oxide obtainable by one of the processes described in the present application.

15

3. Polysaccharide (starch) crosslinked with a dichloropolyethylene oxide as superabsorbent.

4. Use of the crosslinked polysaccharide according to claim 1 as biodegradable superabsorbents and or/and as hypoallergenic superabsorbents.

20

5. Superabsorbent mixture comprising at least one crosslinked polysaccharide according to claim 1.

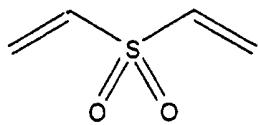


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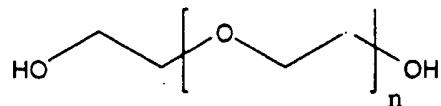


Figure 2

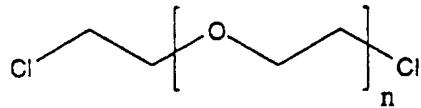


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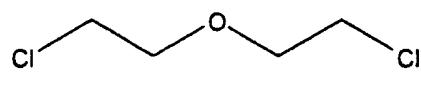


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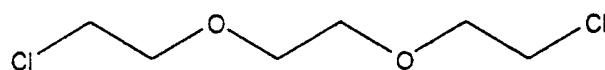


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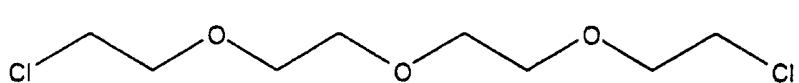
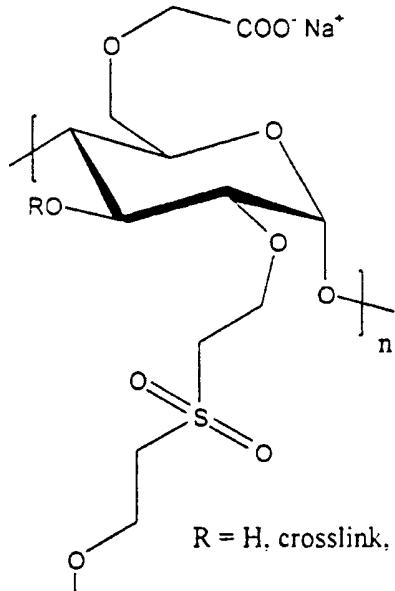
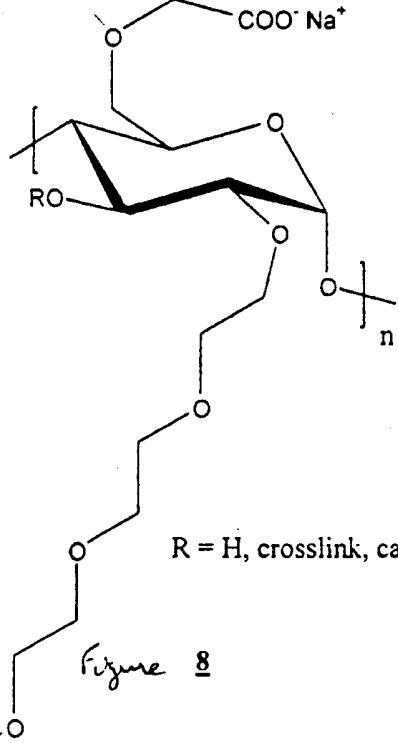


Figure 6



Carboxymethylstarch

Figure 7



Carboxymethylstarch

Figure 8

16

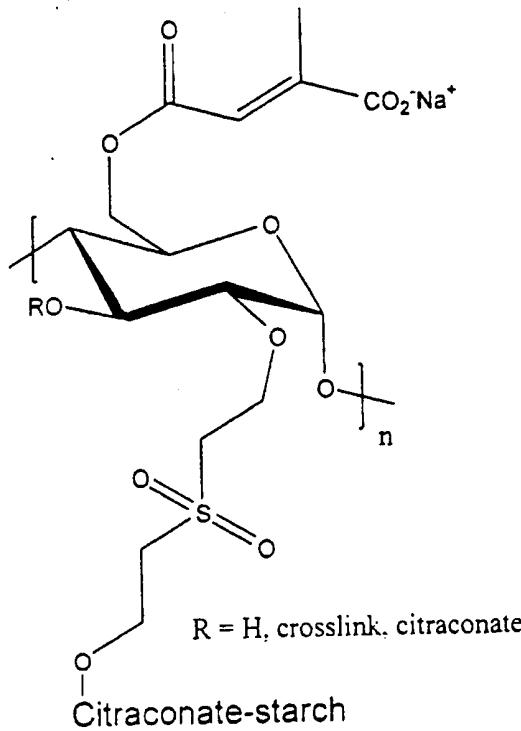


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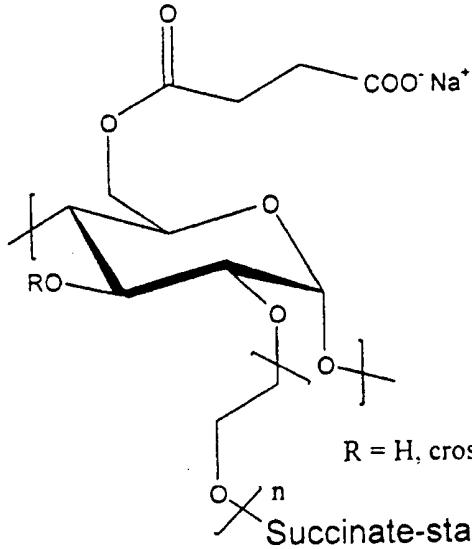
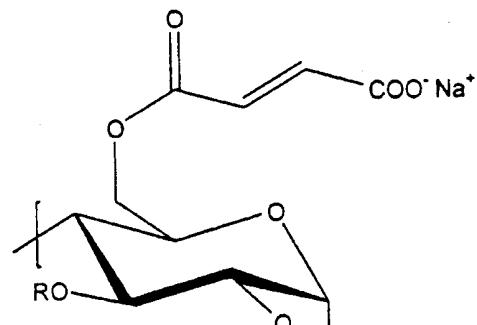
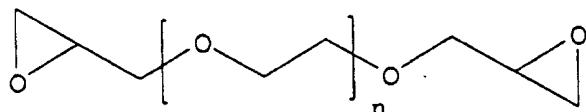
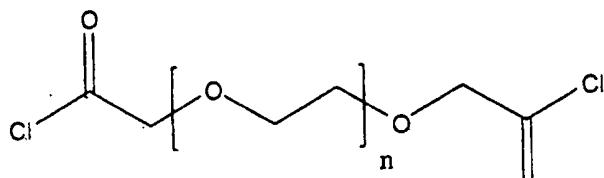
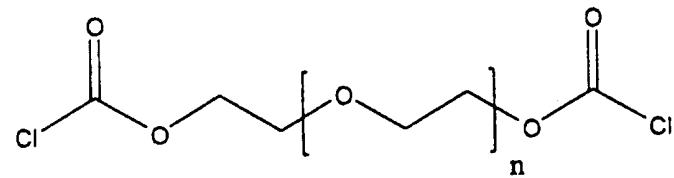
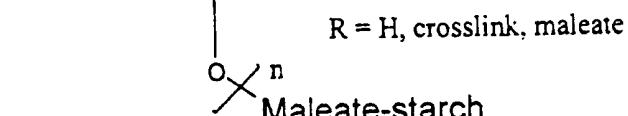


Figure 14

Figure

13



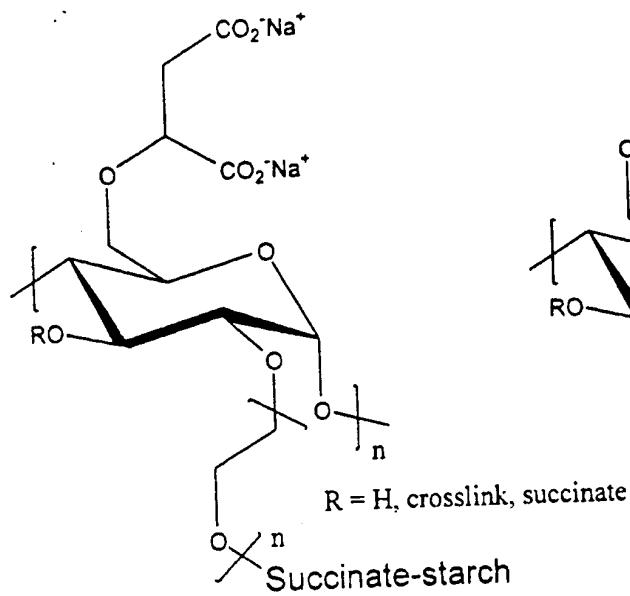


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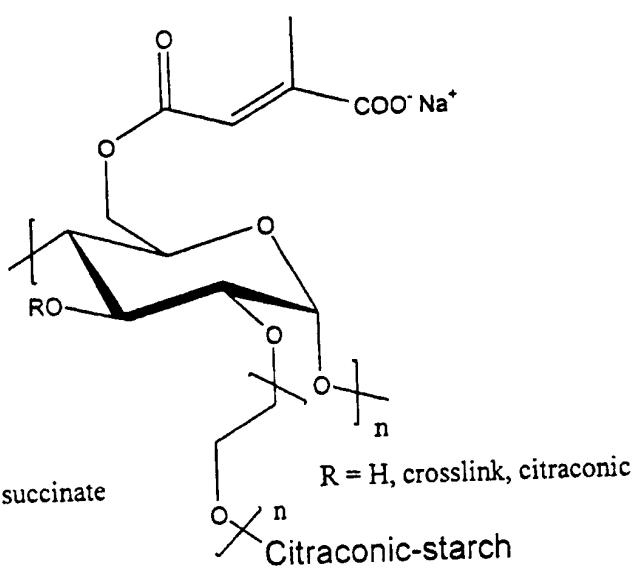


Figure 16

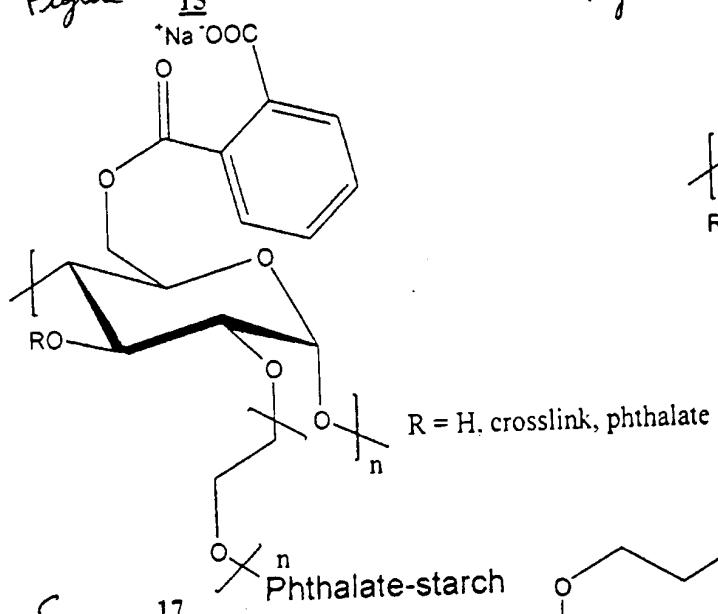


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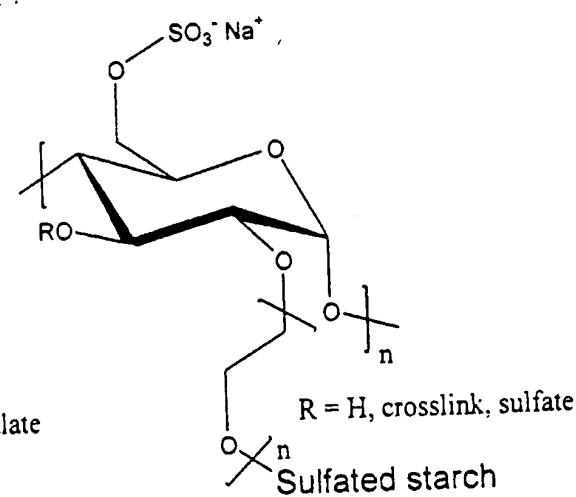


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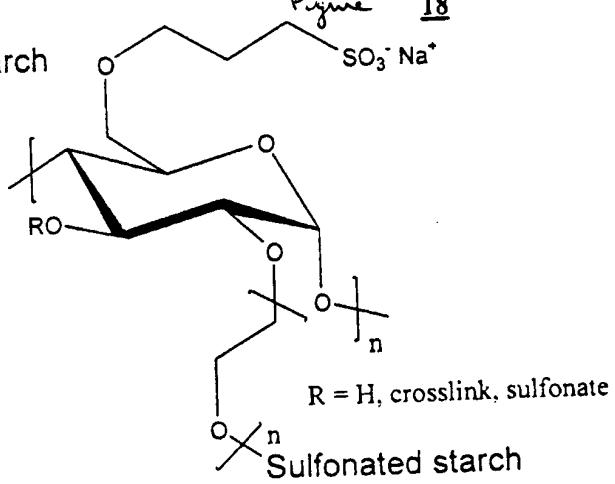


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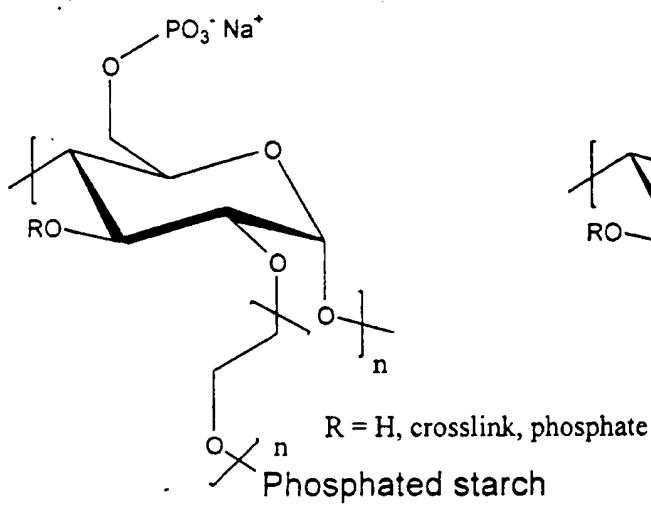


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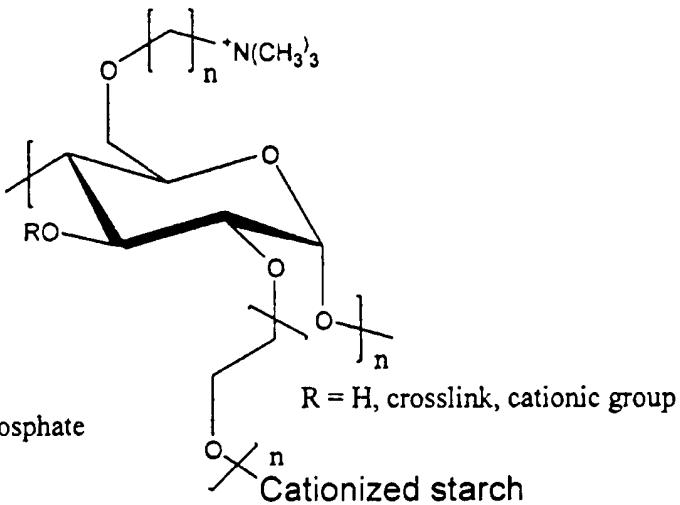


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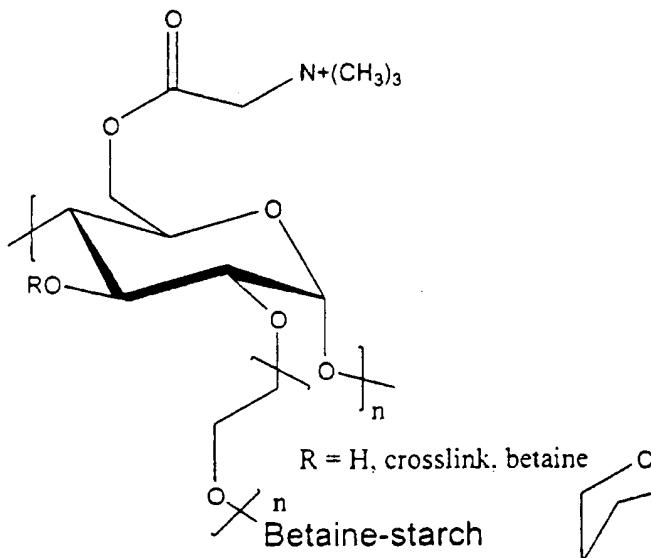


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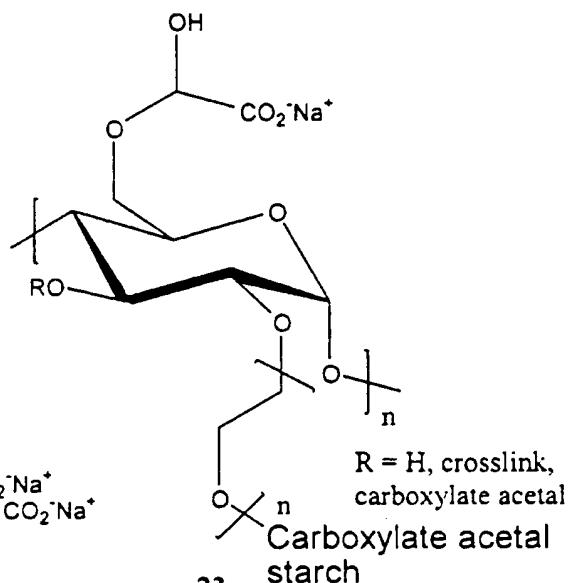


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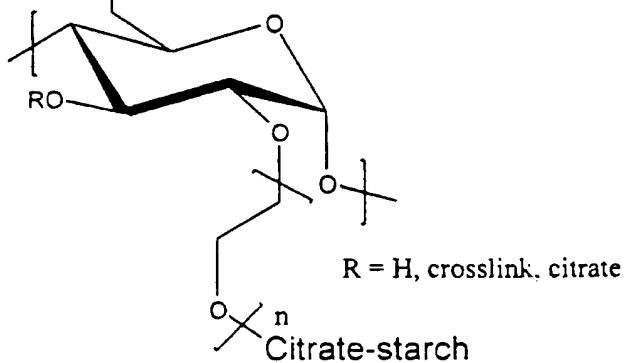


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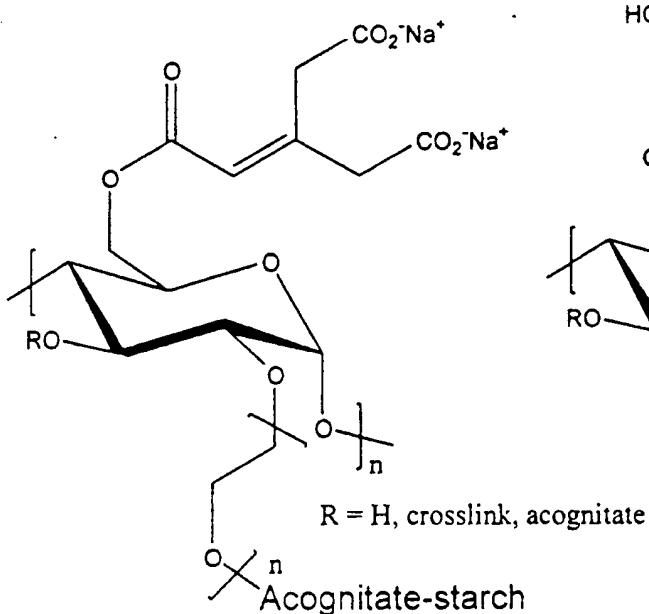


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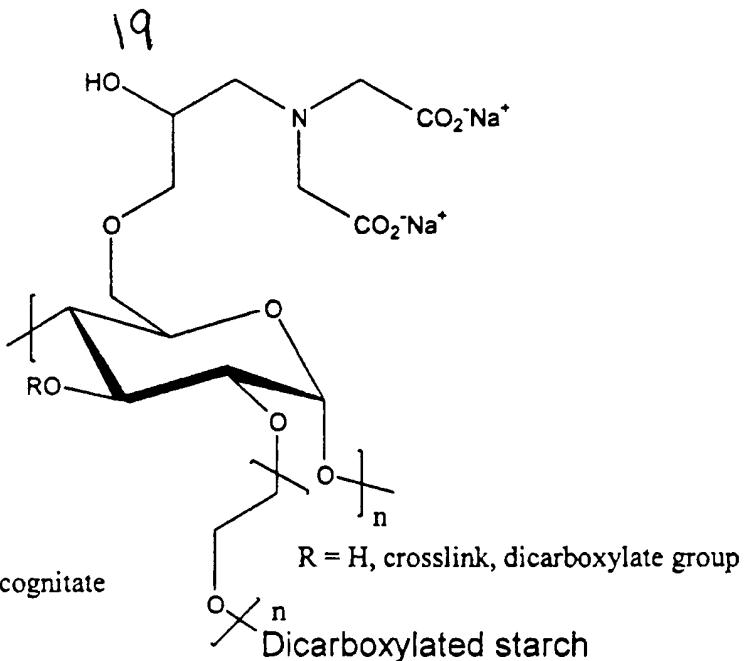


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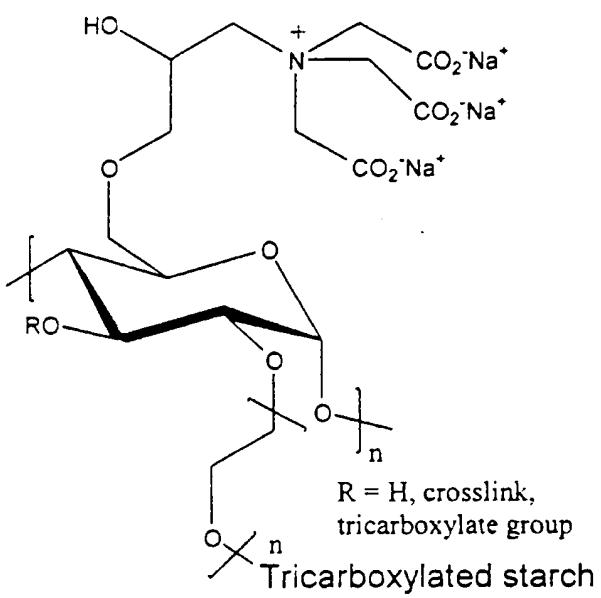


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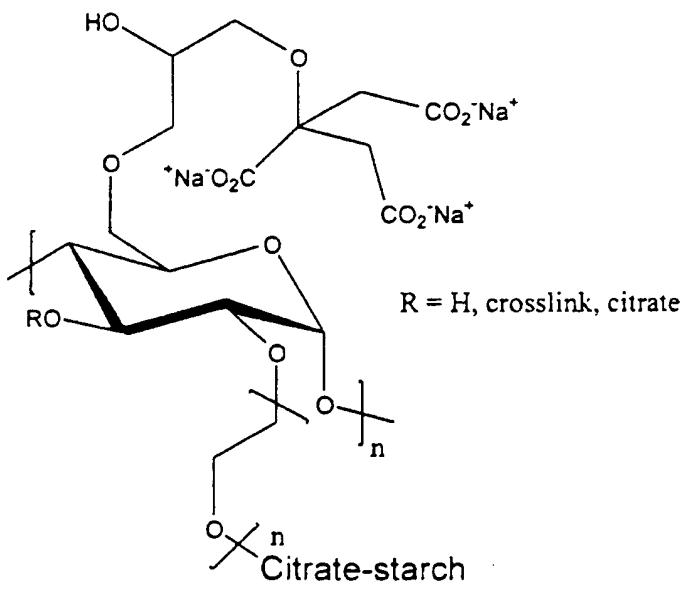


Figure 28

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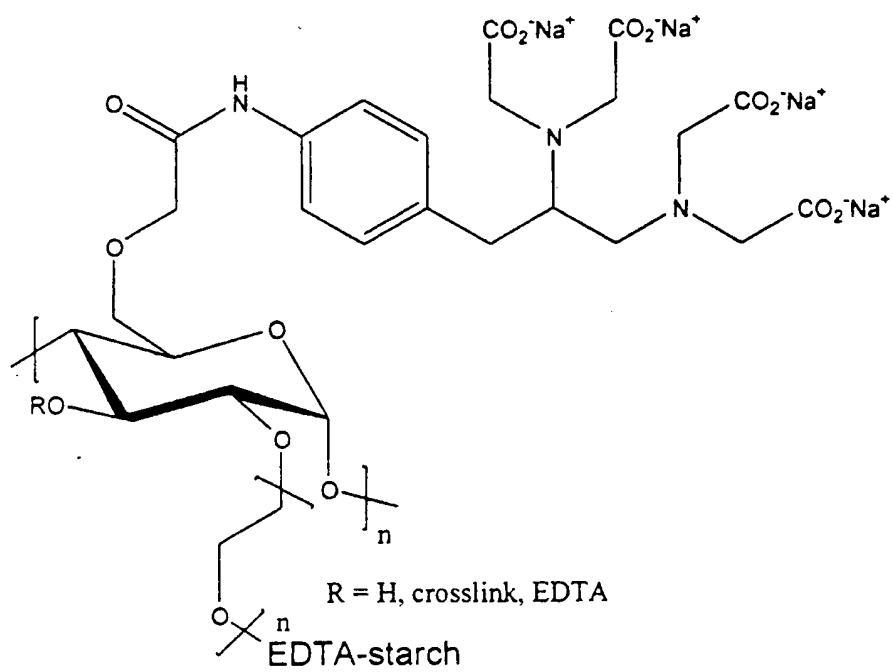


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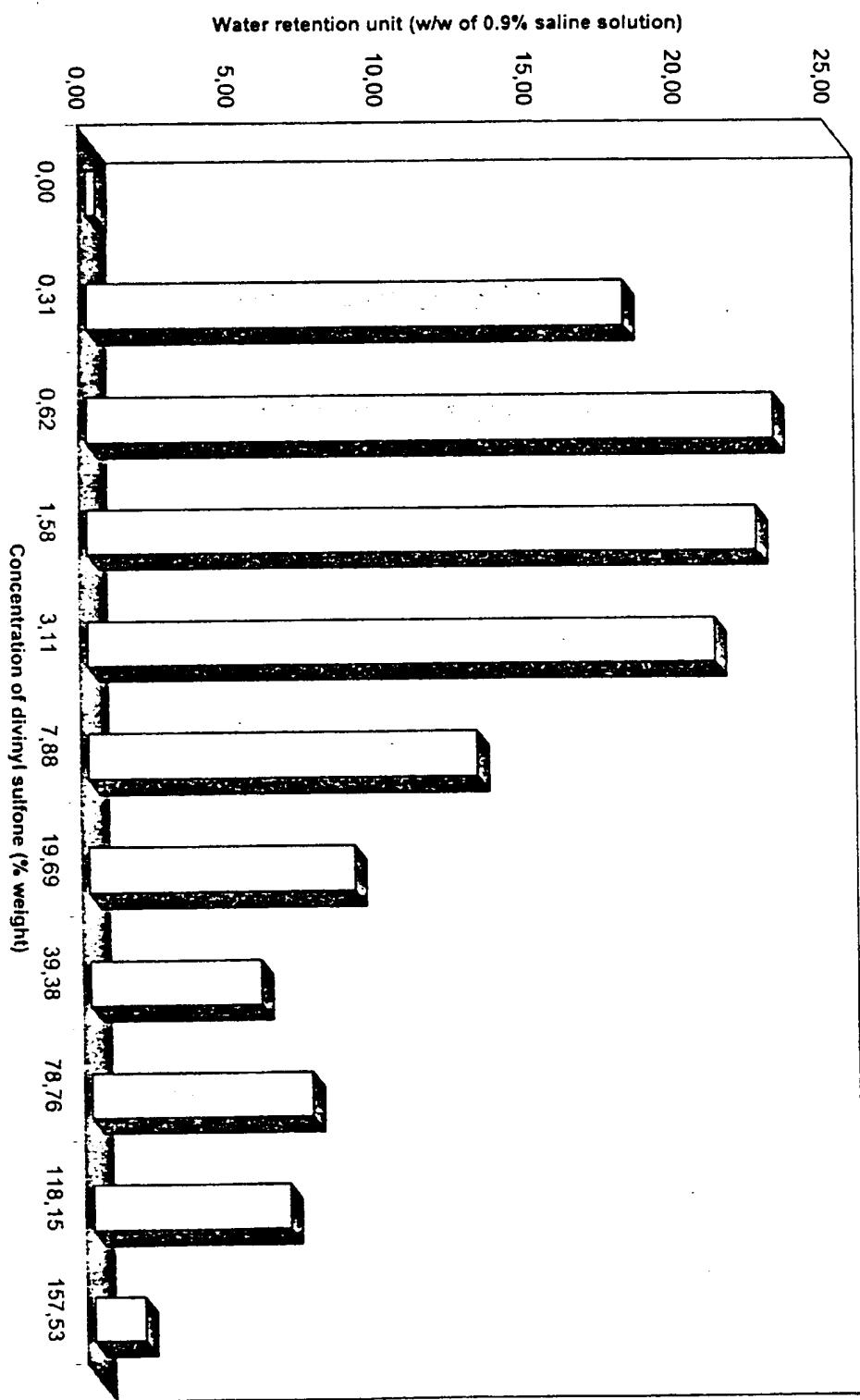


Figure 1. Effect of divinyl sulfone on water retention of carboxymethylstarch.

Figure 3e

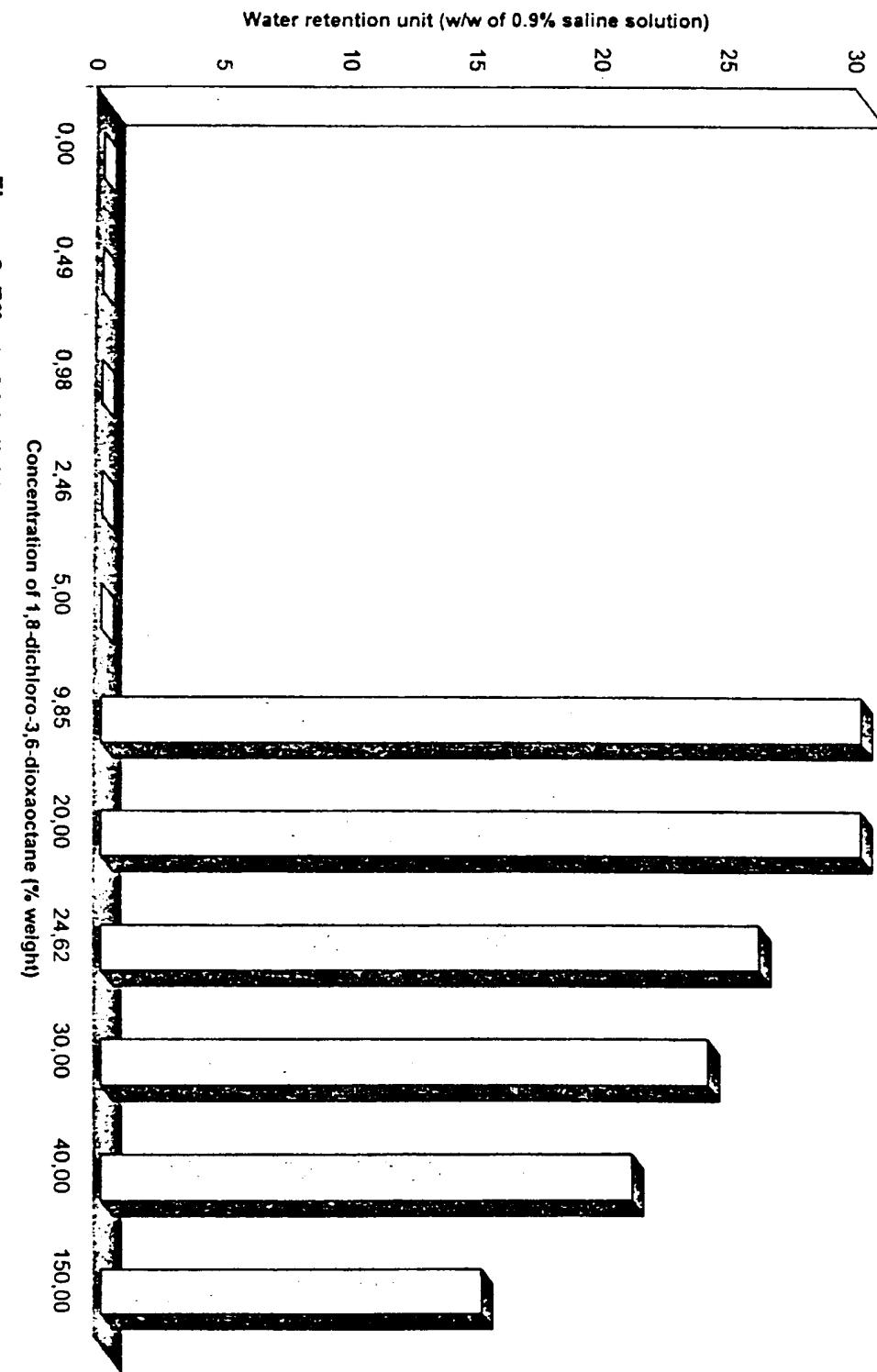


Figure 2. Effect of 1,8-dichloro-3,6-dioxaoctane on water retention of carboxymethylstarch.

Figure 3A